Analysis of Ethanol Reforming System Configurations

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Project ID #: **PD3**

Overview

Timeline

- Contract Period:
  - May 2007 to September 2008
  - 75% complete

Barriers

- Distributed H_2 Production from Renewable Liquids:
  - A: Reformer Capital Costs
  - B: Reformer Manufacturing

Budget

- Total project funding: $150k
- Funding for FY 2007: $150k

DOE Cost Targets

Characteristic	2006	2012	2017
System Efficiency	70%	72%	65-75%
Prod. Unit Capital Cost (uninstalled)	$1.4M	$1.0M	$600k
Total H_2 Cost	$4.40/kg	$3.80/kg	<$3.00/kg

Collaborations

- Interaction/Data-Transfer between PNL, OSU and multiple DOE contractors (H_2Gen, Pall Corp., Virent)

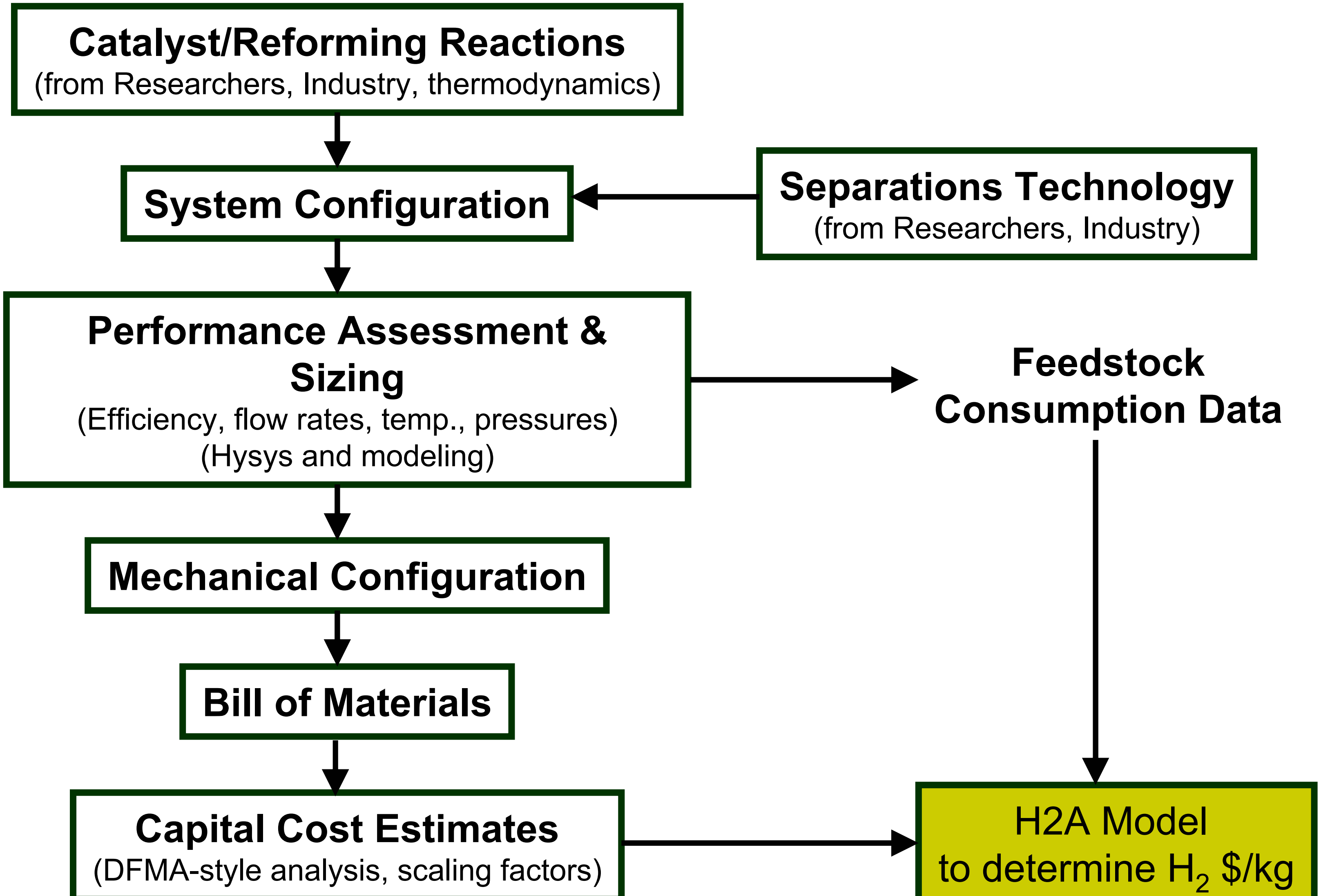
Objectives

- **Assess cost of H_2 from bio-derived liquids**
  - Distributed forecourt scale systems: 1500kgH_2/day
  - Emphasis on Ethanol
  - Both “conventional” and “advanced” systems

- **Reflect Recent Research**
  - Interact with DOE Labs and Contractors
  - Researchers supply catalysts composition, performance, potential configurations
  - Ground in reality but forward looking

- **Output of work is:**
  - System/Configuration Definition
  - Performance specification & optimization
  - Capital cost estimation
  - Projected hydrogen $/kg

Methodology



Ethanol Reforming Hierarchy

Reforming Options

Gas Phase

Steam Reforming

High Temp
>550˚C

"2-Step" Ref.
(ie. methanation followed by SMR)
H_2Gen
With WGS

Med. Temp
300-550˚C

"1-Step" Ref.
PNNL
OSU
With or Without WGS

Partial Oxidation
GE (SCPO)
MRT/Linde (fluidized bed)
With WGS

OTM/ Water-Splitting
ANL
With WGS

Liquid Phase
Virent
(glycerol/sugars feedstock)

H_2 Purification

PSA

Separate Membrane Section

Membrane/WGS

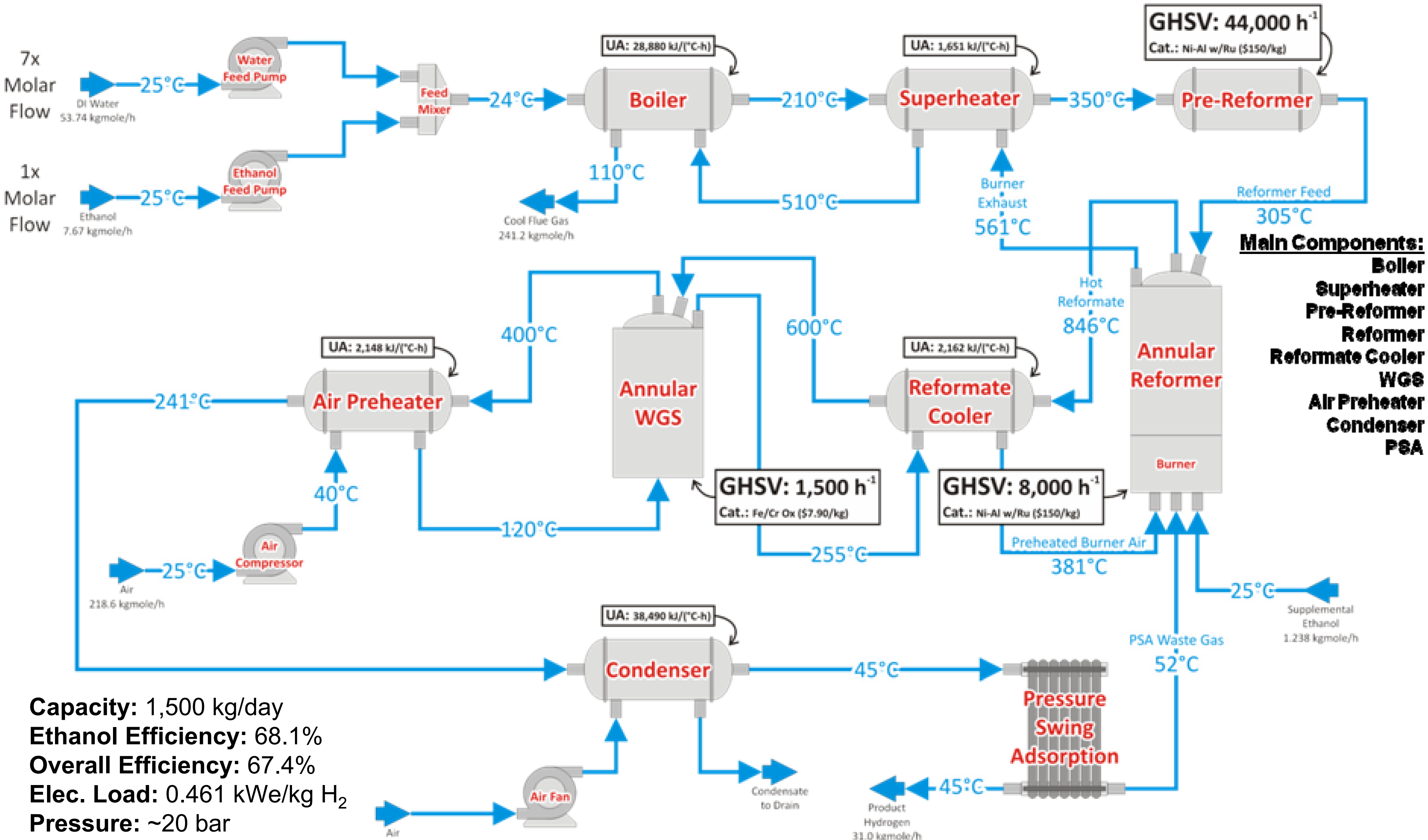
Membrane Reactor

Multiple Configurations Examined

Config. Number	Fuel	Temperature	Key Elements
1	NG	High Temp. (900°C)	SMR → WGS → PSA
2			
14		Med. Temp. (550°C)	Integrated Reformer/WGS/Membrane Separator
6	Ethanol	High Temp. (900°C)	Pre-Reformer → SMR → WGS → PSA
11			Pre-Reformer → SMR → WGS → Membrane Separator
12			Pre-Reformer → SMR → Integrated WGS/Membrane Separator
9		Med. Temp. (550°C)	Reformer (NPM Catalyst) → WGS → PSA
15			Reformer (PM Catalyst) → WGS → PSA
10			Reformer (NPM Catalyst) → Membrane Separator
13			Integrated Reformer/WGS/Membrane Separator

- **Many configurations/variations are possible**
- **Arrows mark focus for today's presentation**

System 06
High Temp. w/ Pre-Reformer & PSA



Capacity: 1,500 kg/day
Ethanol Efficiency: 68.1%
Overall Efficiency: 67.4%
Elec. Load: 0.461 kWe/kg H_2
Pressure: ~20 bar
H_2 Recovery: 75%
Capital Cost: $829,630

System 09

Med. Temp. w/ PSA

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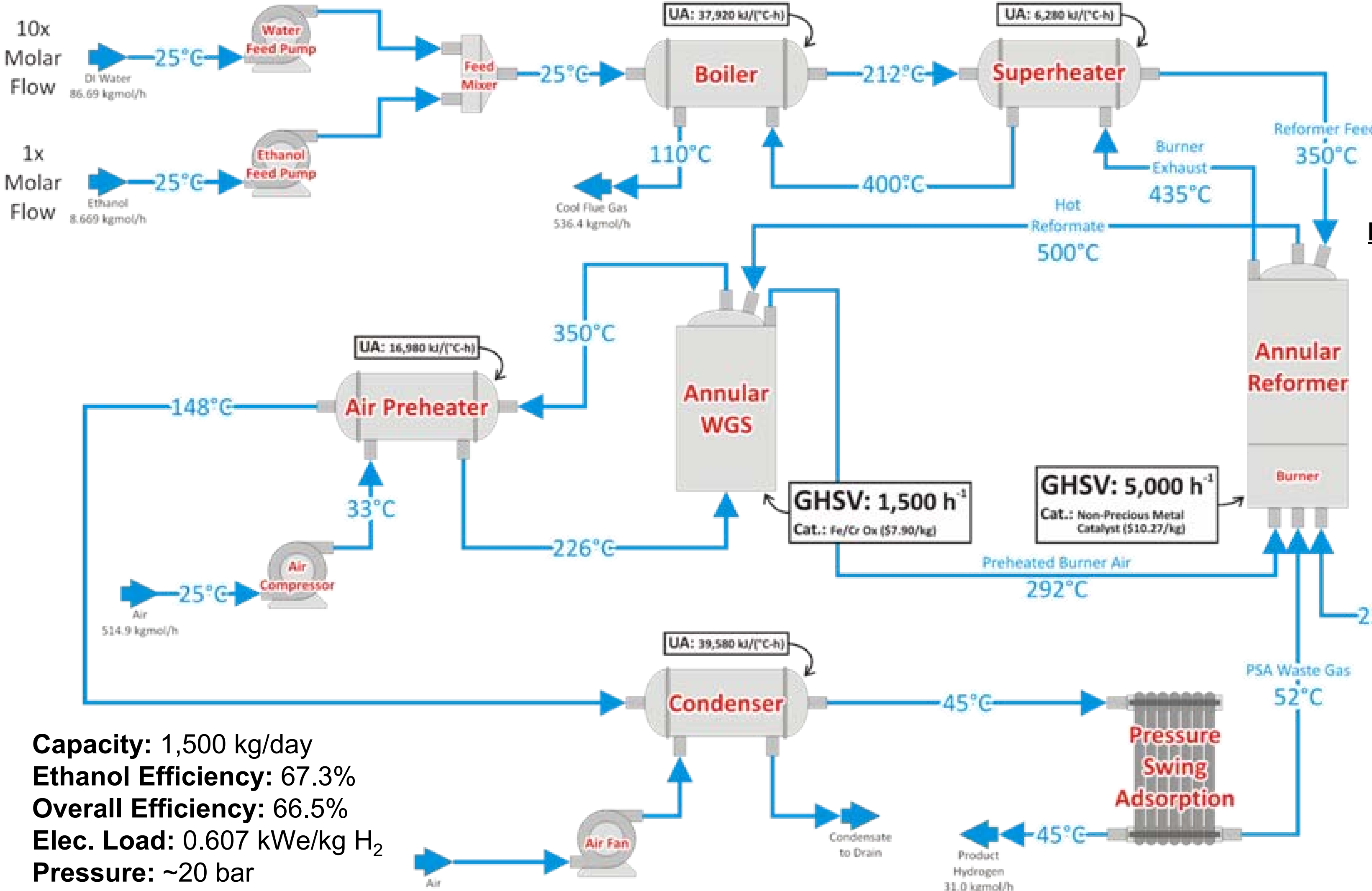
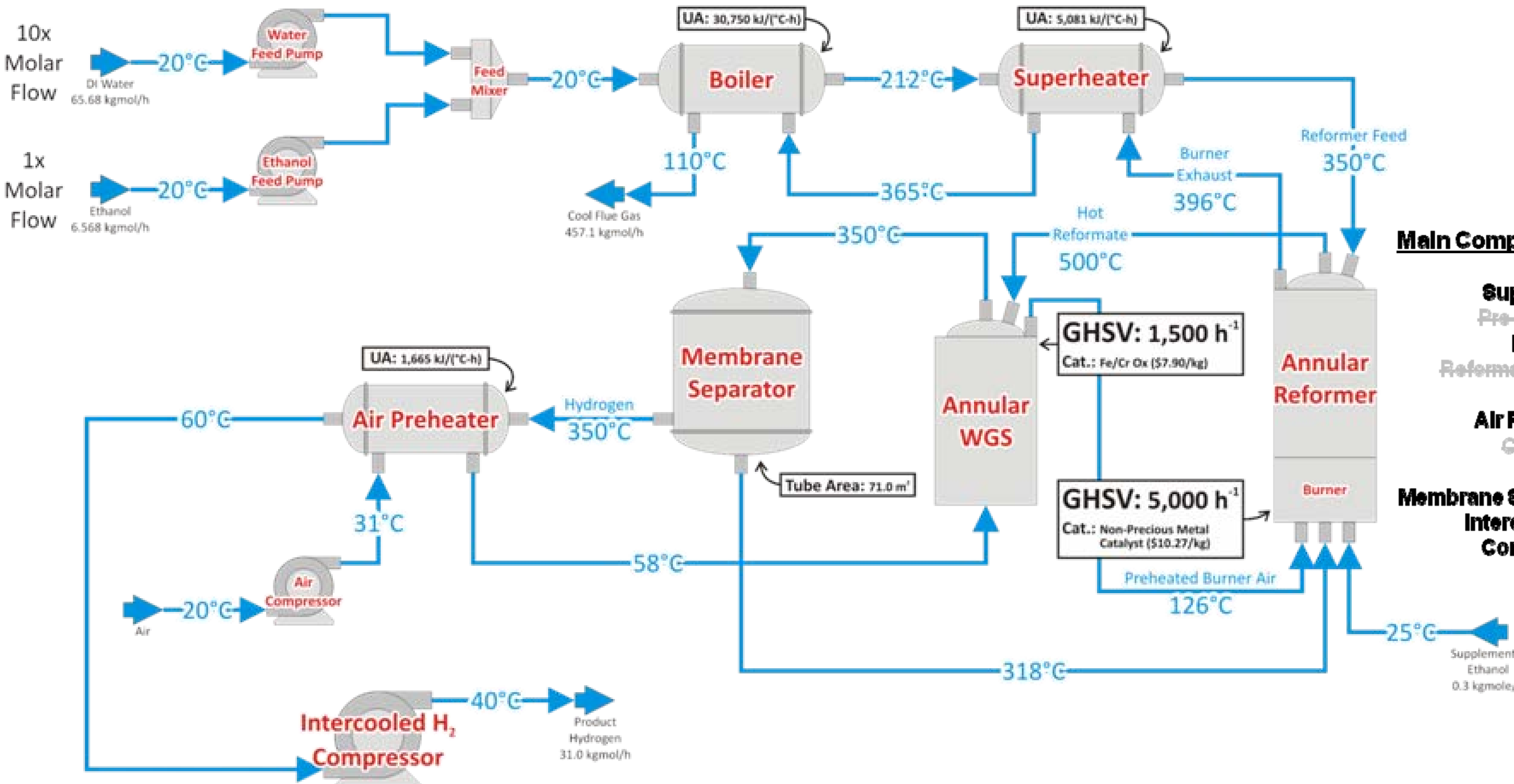


Main Components:
Boiler
Superheater
~~Pre-Reformer~~
Reformer
~~Reformate Cooler~~
WGS
Air Preheater
Condenser
PSA

Capacity: 1,500 kg/day
Ethanol Efficiency: 67.3%
Overall Efficiency: 66.5%
Elec. Load: 0.607 kWe/kg H_2
Pressure: ~20 bar
H_2 Recovery: 75%
Capital Cost: $672,746

System 10

Med. Temp. w/ Membrane Separator



Main Components:
Boiler
Superheater
~~Pre-Reformer~~
Reformer
~~Reformate Cooler~~
WGS
Air Preheater
~~Condenser~~
~~PSA~~
Membrane Separator
Intercooled H_2 Compressor

Capacity: 1,500 kg/day
Ethanol Efficiency: 64.5%
Overall Efficiency: 61.2%
Elec. Load: 2.209 kWe/kg H_2
Pressure: ~20 bar
H_2 Recovery: 90%
Capital Cost: $800,344

System 13a

Med. Temp. w/ Intgr. Membrane Tubes

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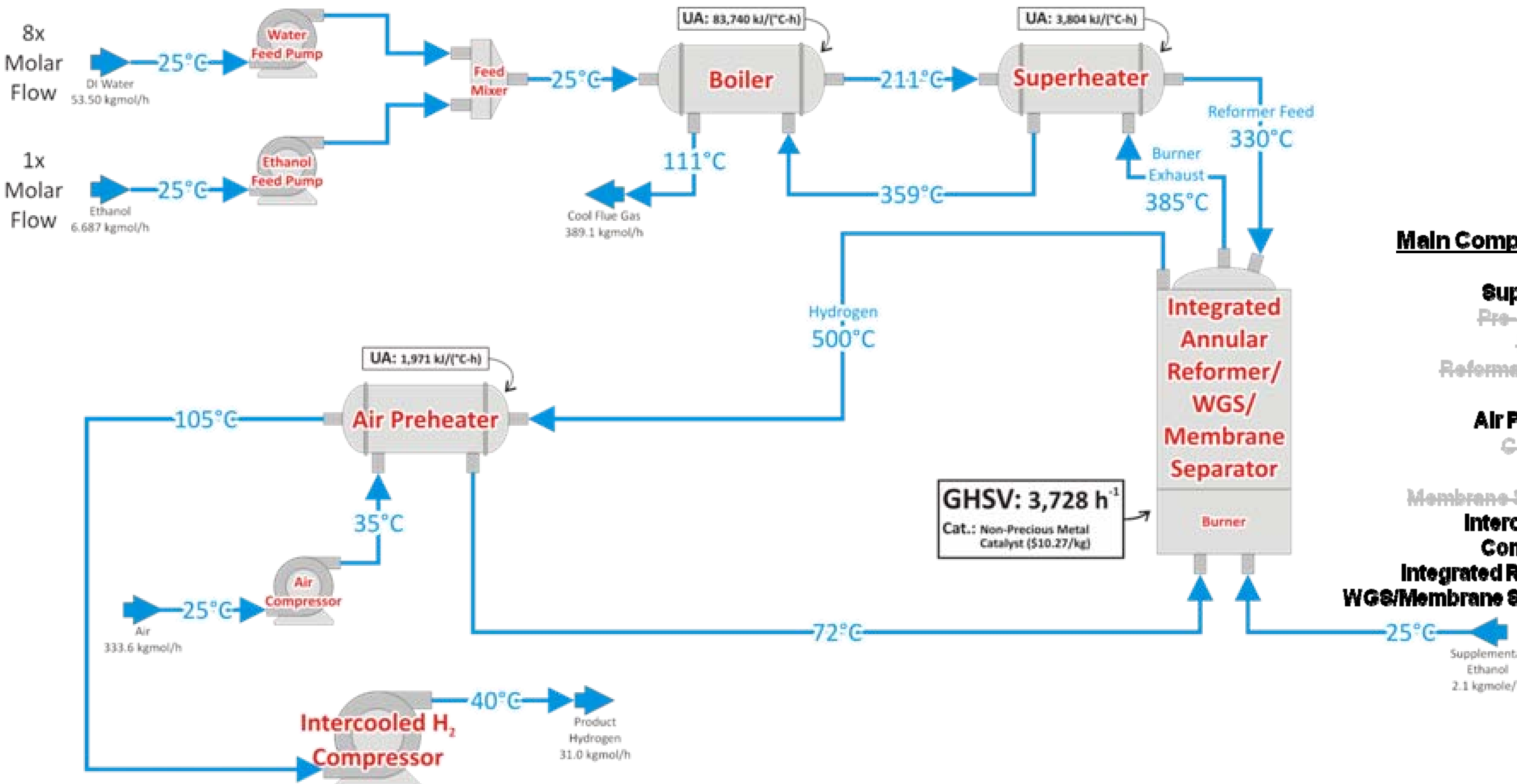

Main Components:
Boiler
Superheater
~~Pre-Reformer~~
~~Reformer~~
~~Reformate Cooler~~
~~WGS~~
Air Preheater
~~Condenser~~
~~PSA~~
~~Membrane Separator~~
Intercooled H_2 Compressor
Integrated Reformer/ WGS/Membrane Separator

Capacity: 1,500 kg/day
Ethanol Efficiency: 69.8%
Overall Efficiency: 67.5%
Elec. Load: 2.064 kWe/kg H_2
Pressure: ~20 bar
H_2 Recovery: 90%
Capital Cost: $711,417

Kinetics Model Used to Determine Bed Sizes

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Reforming Reaction:

$$\text{EtOH Consumption Rate} = C_1 k_0 \exp\left(-\frac{E_A}{RT}\right)\left(P_{C_2H_5OH}\right)^{1.25}\left(P_{H_2O}\right)^{-0.215}$$

where
k_0 = 0.013 mol/(gcat·s·kPa$^{1.07}$)
E_A = 39.3 kJ/mol
C_1 = Derating Factor = 38%-49%

- From E. Örücü, F. Gökaliler, A. E. Aksoylu, Z. I. Önsan (2008) *Ethanol Steam Reforming for Hydrogen Production Over Bimetallic Pt-Ni/Al_2O_3*, J Catalysis Letters Vol. 120, No. 3-4, Jan. 2008, Springer Netherlands, pp 198-203
- Derating Factor selected based on PNNL (King et al) and OSU (Ozkan) data.

Representative Data:

	Precious Metal PNNL (King)	Non-Precious Metal OSU (Ozkan)
Steam/Ethanol Ratio	8:1	10:1
GHSV	5,786/h for long life	5,000/h
Ethanol Conversion	99%+	99%+
Temperature	550°C	550°C
Catalyst	2wt%Rh/ $Ce_{0.8}$Zr0.2O2	1%Ni-1%Cu-10%Co/$Ca_{0.1}Ce_{0.9}O_{1.9}$
Exit Gas Composition:		
H_2	71.12%	71.50%
CH_4	4.67%	3.80%
CO	5.38%	4.10%
CO_2	18.83%	20.60%
Ethylene	0%	0%
Ethane	0%	0%

WGS Reaction:

$$\text{CO Consump. Rate} = C_2 \exp\left(-\frac{E_A}{RT}\right)[CO]^1$$

where
E_A = 121.8 kJ/mol

DOE Tech. Targets for Dense Metallic Membranes

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Flux Rate:	2006 Status	2010 Target	2015 Target
	>200 scfh/ft^2	250 scfh/ft^2	300 scfh/ft^2

Based on:

- 20 psi partial pressure difference
- 15 psig permeate minimum total pressure (preferably >50 psig) (assumed to be pure H_2)
- 400°C

Sievert's Law

$$D = A \cdot \mathcal{P} \cdot (P^{0.5}_{H_2\ \text{Reformate}} - P^{0.5}_{H_2\ \text{Permeate}})$$

where permeability, $\mathcal{P} = \dfrac{a}{t} e^{\frac{-b}{RT}}$

where

D is the hydrogen permeation rate in **scfh**

$\mathcal{P}$ is the permeability, in **scfh/ft^2/atm$^{0.5}$**

A is the membrane effective surface area in **ft^2**

P_{H_2} is the hydrogen partial pressure (reformate or permeate streams) in **atm**

t is the thickness of the membrane in **ft**

T is the membrane temperature in **°R**

R is the ideal gas constant in **ft^3-atm/°R/lb-mol**

a, b are the empirical constants dependent on the material of the membrane

Therefore implied Permeability Technical Targets are:

Permeability:	2006 Status	2010 Target	2015 Target
	>454 scfh/ft^2/atm$^{0.5}$	567 scfh/ft^2/atm$^{0.5}$	>680 scfh/ft^2/atm$^{0.5}$

Modeling Stand-Alone Membrane Separators

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Membrane Separation Unit Sizing Model

Directed Technologies, Inc.
Jeff Kalinoski
1/2/2008

Permeance:	567	scf/(hr*ft^2*atm$^{0.5}$)
Initial System Molar Flow Rate:	71.78	kg-mol/hr
Inner Tube Diameter:	1.27	cm
Inner Tube Diameter:	0.5	in
Number of Tubes:	100	
Δt:	0.001	s
Cross-Sectional Area of Tube:	1.2668	cm^2
Cross-Sectional Area of Tube:	0.19635	in^2

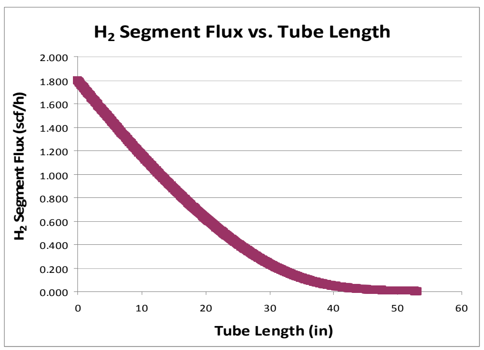
Constant Δt, variable Δx

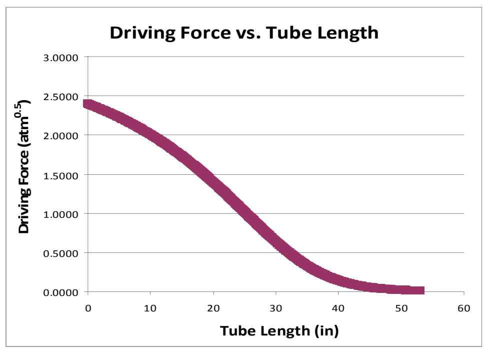
SCF Conditions:			STP Conditions:			Actual Conditions:		
Density of H_2:	0.00531	lb/scf	Volume:	22.414	L/g-mol	Reformate Pressure:	20	atm
Temperature:	60	°F				Permeate Pressure:	1	atm
			Temperature:	0	°C	Temperature:	400	°C
			Temperature:	491.67	°R	Temperature:	859.670	°R
			Pressure:	1	atm	lb of H_2/lb-mol:	2.016	

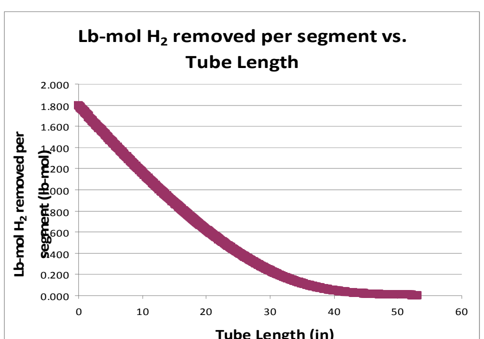
	CO	CO_2	CH_4	H_2O	H_2	Other
Mole Fract	0.0034	0.158	0.0176	0.324	0.497	0

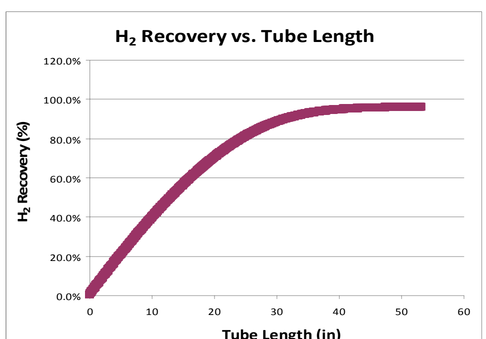
speed	x	t	Initial Molar Flow Rate	Initial Molar Flow Rate	Initial Molar Flow Rate	Volumetric Flow Rate	Volumetric Flow Rate	Segment Volume	Segment Length	Segment Surface Area	Segment Surface Area
in/s	in	s	kg-mol/hr	lb-mol/hr	lb-mol/s	L/hr	ft^3/s	in^3	in	in^2	ft^2
	0	0.000	0.7178	1.5825	0.00044	1,406.54	0.0138	0.02	0.1214	0.19	0.00
121.428	0.12	0.001	0.7156	1.5777	0.00044	1,402.32	0.0138	0.02	0.1211	0.19	0.00
121.246	0.24	0.002	0.7135	1.5730	0.00044	1,398.13	0.0137	0.02	0.1207	0.19	0.00
121.064	0.36	0.003	0.7114	1.5683	0.00044	1,393.95	0.0137	0.02	0.1203	0.19	0.00
120.884	0.48	0.004	0.7093	1.5636	0.00043	1,389.80	0.0136	0.02	0.1200	0.19	0.00

x	CO		CO_2		CH_4		H_2O		H_2		Other	
	Mole Fraction	Pound-Moles	Mole Fraction	Pound-Moles	Mole Fraction	Pound-Moles	Mole Fraction	Pound-Moles	Mole Fraction	Pound-Moles	Mole Fraction	Pound-Moles
in	%	lb-mol	%	lb-mol	%	lb-mol	%	lb-mol	%	lb-mol	%	lb-mol
0	0.63%	2.769E-09	14.3%	6.304E-08	3.26%	1.433E-08	24.1%	1.06E-07	57.7%	0.0000003	0.0%	0
0.12	0.6%	2.769E-09	14.4%	6.304E-08	3.3%	1.433E-08	24.2%	1.06E-07	57.5%	0.000	0.0%	0
0.24	0.6%	2.769E-09	14.4%	6.304E-08	3.3%	1.433E-08	24.2%	1.06E-07	57.4%	0.000	0.0%	0
0.36	0.6%	2.769E-09	14.5%	6.304E-08	3.3%	1.433E-08	24.3%	1.06E-07	57.3%	0.000	0.0%	0
0.48	0.6%	2.769E-09	14.5%	6.304E-08	3.3%	1.433E-08	24.4%	1.06E-07	57.2%	0.000	0.0%	0







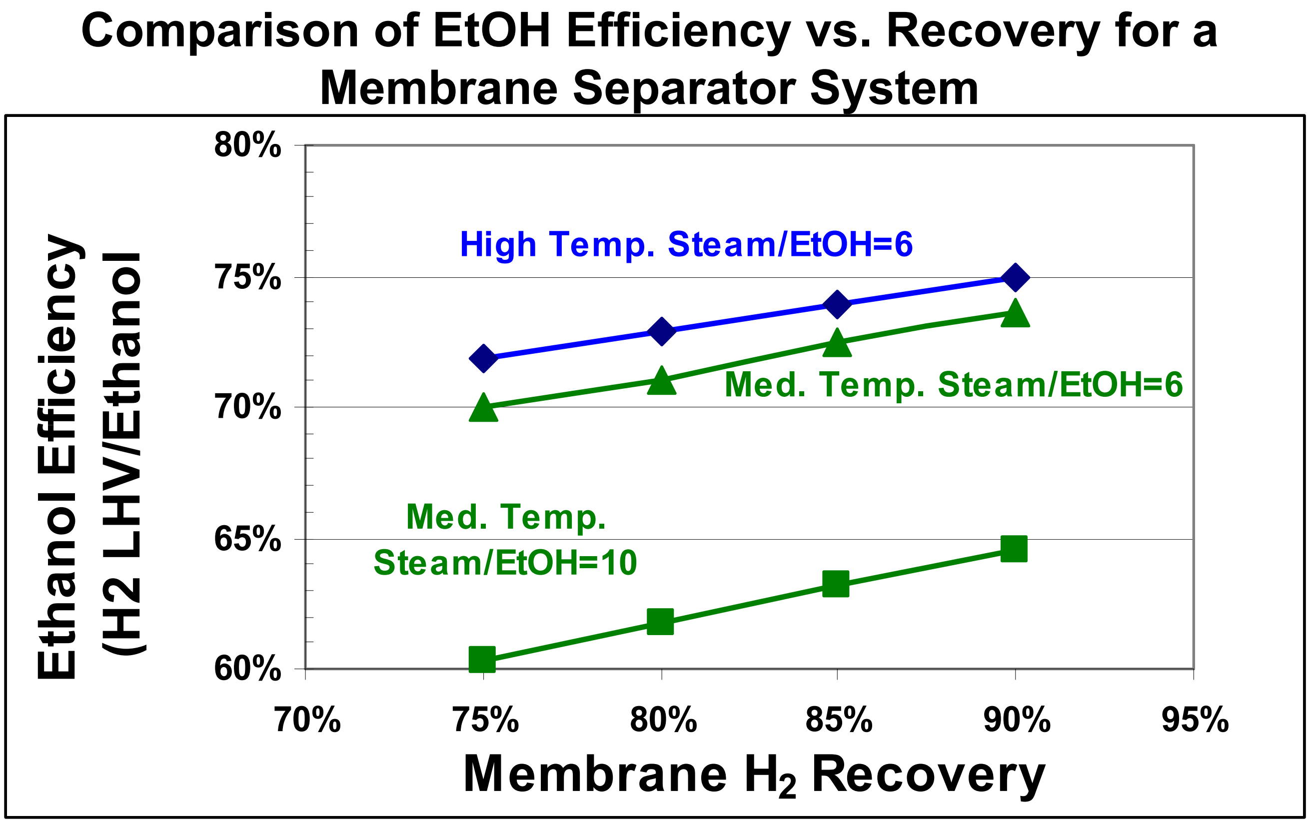


- 1-D Differential Element Separation Model Created (Excel Based)
- No reaction chemistry
- Assumed 100% selectivity (i.e. metal membrane)
- Used to determine membrane area for stand-alone Membrane Separator
- Permeance based on 2010 DOE Targets

Typical Parameters for a 1500kgH_2/day Separator

Inlet Presure	20 atm
Permate Pressure	1 atm
Inlet Molar Flow	83 kgmol/h
Inlet H2 Molar Fraction	41%
Permeance	567 scfh/ft^2/atm$^{0.5}$
Membrane Area Required	48 ft^2
H2 Recovery	90%
Cost at \$1000/ft^2	\$48,000

System Level Evaluation is Critical



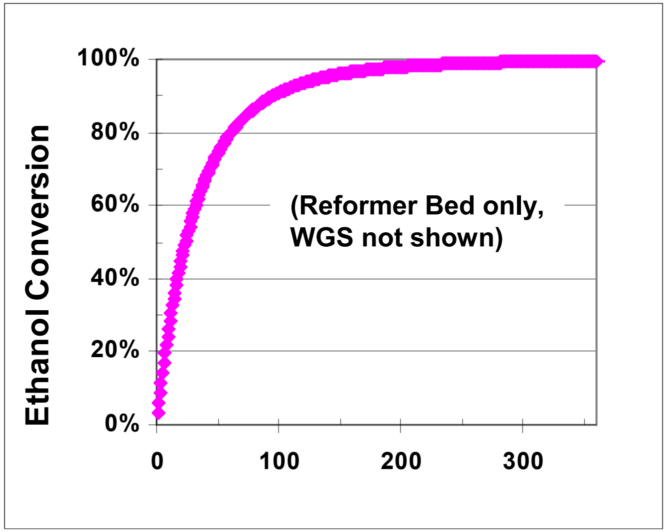
- Steam/Ethanol Ratio has a larger effect than H_2 Recovery

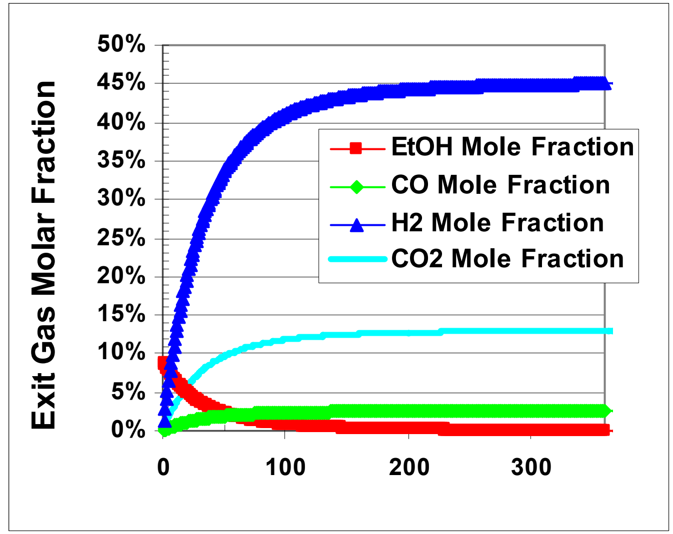
Other considerations:

- Peak membrane temperature ~500-550°C (for Pd-based membranes)
- Membrane H_2 flux increases with temperature
- Membrane area increases with Recovery and H_2 Dilution

Impact of Integrated Membrane On Overall Catalyst Bed Size

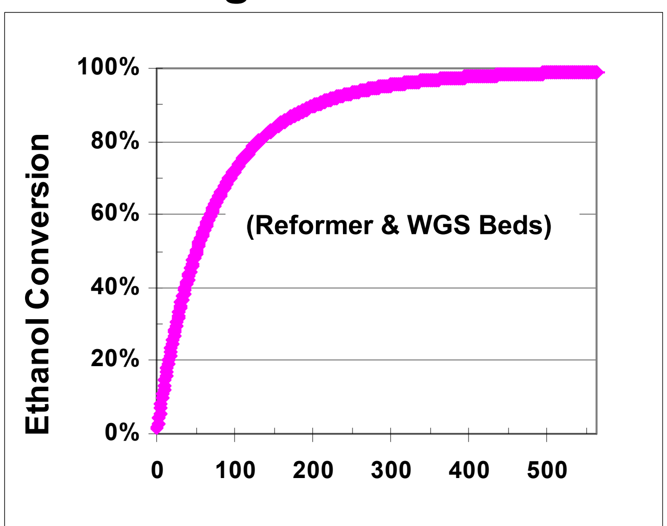
Discrete Reactors (Reformer→WGS →PSA) (Sys 9)

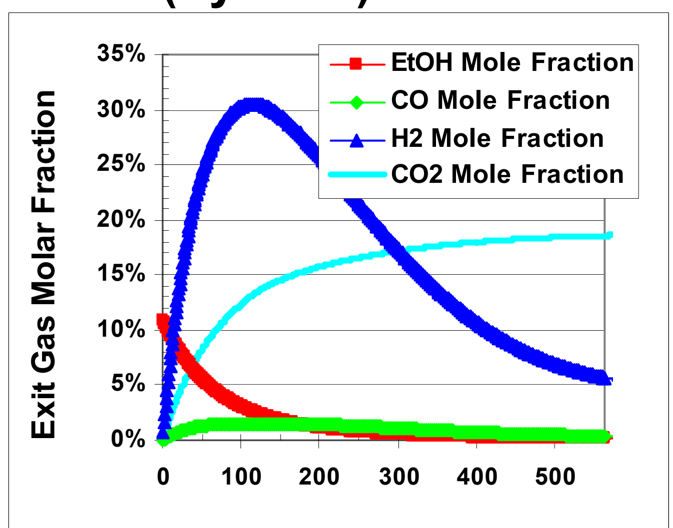




- Near-complete EtOH conversion (99%+)
- But requires separate WGS Reactor and Gas Cleanup System

With Integrated Ref/WGS/Membrane (Sys 13a)





- Also good EtOH conversion
- Combines Reformer/WGS/ Membrane into single unit
- <1/4 the total bed volume

Two Reactor Configurations Examined

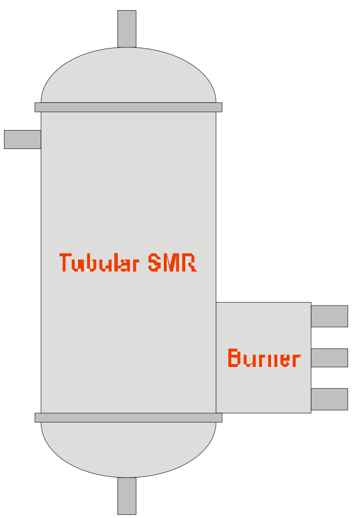
Tubular Reactor

- Excellent heat transfer if small diameter tubes
- But small diam. tubes → unwieldy # of tubes
- Configuration not amenable to membrane tubes

Annular Heat Exchange Reactor (HER)

- Simpler design - fewer parts
- Amenable to membrane system integration
- ~25% lower cost than Tubular

Annular Design Selected for Design Studies



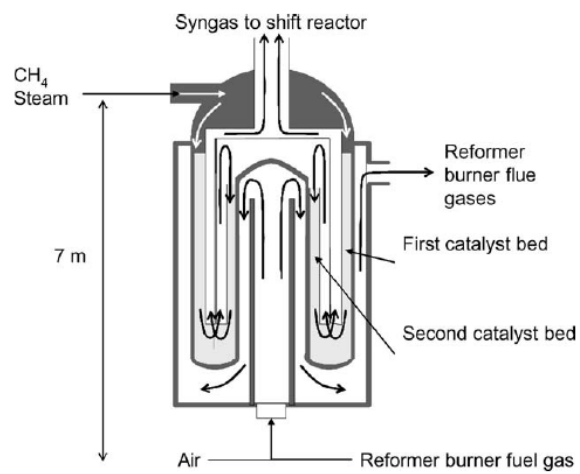
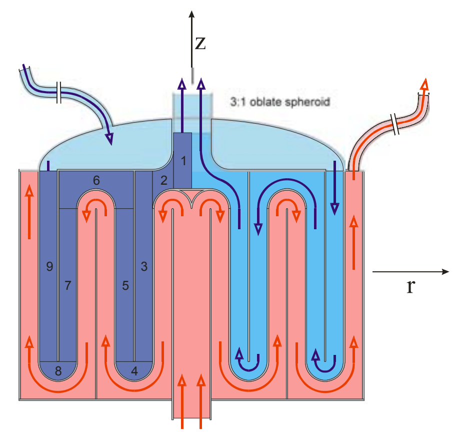


Figure 18: Heat exchange reformer (HER) with annular concentric catalyst bed (170).



[170] Topsoe HTCR Compact Hydrogen Units. Haldor Topsoe A/S. www.haldortopsoe.com (accessed Dec. 2004).

Key Assumptions and Observations

- **All Systems sized for 1,500 kgH_2/day**
- **All catalyst systems assumed to have 5 year life**
  - Precious Metal Catalysts have approx. shown multi-year life
  - Non-Precious Catalysts have shorter lifetimes
- **Membranes are assumed to operate with 1atm H_2 permeate pressure**
  - Cost of H_2 Compression is significant (~$200k per H2A projection)
  - Compressor costs mostly off-sets capital cost gain of integrated reformer
- **DOE 2010 Membrane Performance and Cost Targets Assumed**
  - Flux: 250 scfh/ft^2 (at prescribed conditions)
  - Module Cost: $1,000/ft^2
- **H2A Forecourt Spreadsheet Used for all $/kg projections**
  - Version 26: February 2008
- **Steam-to-Carbon and Steam-to-Ethanol Ratios cause confusion**
  - Because ethanol is C_2H_5OH there is a 2x difference in the ratio
  - S/C=4 is the same as S/Ethanol=8

Modeling Results

Case #	Description	Ethanol Efficiency (H_2 LHV/ Ethanol LHV)	Uninstalled Capital Cost $	Production Cost $/kg	Total Cost (Production/ Storage/Disp.) $/kg
	Baseline EtOH (High Temperature, Pre-Reformer)				
6	- with PSA (75% H2 Recovery)	68.1%	$830k	$3.02/kg	$5.04
11	- with Membrane Separator (90% H2 Recovery)	74.9%	$909k	$2.96/kg	$4.98/kg
	Medium Temperature EtOH (Steam/EtOH = 8 (PM) /10 (NPM) unless otherwise specified)	PM= Precious Metal Catalyst NPM= Non-Precious Metal Catalyst			
9 15	- with PSA (75% H2 Recovery)	67.3% (NPM) 67.5% (PM)	$673k $839k	$2.95/kg $3.04/kg	$4.97/kg $5.06/kg
10 17	- with Membr. Sep.(90% Recov.)	64.5% (NPM) 66.8% (PM)	$800k $905k	$3.28/kg $3.25/kg	$5.30/kg $5.27/kg
13a 13d	- with Integrated Reformer/WGS/Membrane System	69.8% (NPM) (Steam/Eth.= 8) 67.6% (PM)	$711k ($10/kg catalyst) $929k ($400/kg catalyst)	$3.02/kg $3.23/kg	$5.04/kg $5.25/kg
13b	- Future Integrated Reformer/WGS/Membrane System	79.4% (NPM) (Steam/Eth.= 6)	$608k ($10/kg catalyst)	$2.67/kg	$4.69/kg

Summary

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- Medium & High temperature EtOH reforming are efficiency competitive
- Alternative configurations to tubular designs may lower capital cost
  - but must have adequate heat transfer
- Low Steam/Ethanol ratios favor high system efficiency
  - but must not coke
- Methane in reformer exhaust should be minimized
  - each CH_4 in exhaust robs $4H_2$ from product
  - Methane make is key catalyst evaluation metric
- Catalyst cost is a key cost component. Worthwhile to explore reduced/non precious metal catalysts
  - but must have multi-year lifetimes
- 90% H_2 Recovery in a membrane separator is feasible (at 20atm/1atm)
- Membrane systems (with high recovery) can make significant efficiency improvements (up to 5%)

Summary (continued)

- Mid 70's % LHV Ethanol efficiencies are possible
- H_2 Production Cost of <$3/kg is feasible
- But forecourt compression/storage/dispensing is currently very costly ($2/kg$H_2$)
  - ➢ DOE targets for compression/storage/dispensing need to be met to achieve overall H_2 cost target of <$3/kg
- Integrated reformers have the advantages of:
  - reduced operating temperature
  - lower capital cost
  - lower H_2 $/kg
  - ➢ While cost & efficiency advantage is not decisive, integrated systems are compact & simpler: important for forecourt installation
- Aqueous phase reformers using low cost feedstocks offer a potential pathway to low H_2 cost. Advantages include:
  - low operating temperature
  - low capital cost
  - variety of low cost feedstocks
  - ➢ Cost/Performance analysis is underway

Future Plans

- Complete System Comparisons
- Examine Aqueous Reforming System
- Write Final Report